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(56) Documents Cited

GB 1595061 A GB 1464375 A GB 1438462 A

US 5538612 A US 5521029 A US 4898785 A

US 4861680 A US 4595822 A US 4395432 A

US 4194022 A US 3330707 A

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(54) Conductive coating of titanium suboxide

(57) A titanium suboxide of known stoichiometry is applied to a substrate by a thermal process to form a coating of the same composition. The thermal process may be plasma spraying or laser coating, and the formed article may be an electrode of enhanced corrosion resistance and electrical conductivity. The titanium suboxide has the formula TiO_x where x is 1.5 to 1.95 and forms a coating of substantially the same stoichiometry. Minor amounts of dopant material may be included eg Pt, Iv Ta, Nb, Ru, V, SnO_2 . Alternatively such an additive may be applied by electroplating or thermal stove-coating. The coating process may be carried out under vacuum or under a shield of inert gas.

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METHOD OF APPLYING
CONDUCTIVE COATING

The invention relates to a method for the formation of a corrosion resistant electrically conductive coating on a substrate. The substrate may be an electrode, for say an electrochemical cell.

It has been realised that titanium suboxides are useful as coatings. It is also known that a layer of such a material may be formed on a substrate by flame spraying or plasma spraying, see e.g. GB-A-1438462; US-A-5225382; and GB-A-1595061. In these disclosures mixtures which are precursors for titanium suboxide are plasma sprayed on to a substrate under conditions selected to form the suboxide. Typically the suboxides are of the formula TiO_x where x is between 1.95 and 1.99, see e.g. GB-A-1438462 and US 5225382. While such suboxides are corrosion resistant, their electrical conductivity is not acceptable.

US-A-4252629 discloses a corrosion resistant carrier consisting of sintered TiO_x where x is 0.25 to 1.5 having a coating of manganese dioxide. The carrier can be made by plasma spraying the titanium oxide under argon.

EP-A-0047595 discloses that bulk titanium suboxide of the formula TiO_x where x is 1.55 to 1.95 has corrosion resistance and electrical conductivity. The disclosure teaches that the material may be formed into shapes by pressing or extrusion.

It has now been discovered that if a material of known stoichiometry is applied to a substrate one can obtain a coating of predetermined composition and which has a particularly enhanced corrosion resistance and electrical conductivity.

According to the invention in one aspect there is provided a method of forming a corrosion resistant electrically conductive coating on a substrate, comprising forming a predetermined titanium suboxide of the formula TiO_x where x is 1.55 to 1.95 and then applying that material on to the substrate to form a coating of the same substantially stoichiometry on the substrate.

The material may be applied by any suitable application technique which will not affect the stoichiometry of the material. Such techniques include plasma spraying and laser coating. De-gun coating in which the material is melted and then projected by detonation and other thermal coating techniques may also be considered.

Because the starting material is of a known stoichiometry having desired properties one can obtain directly a coating of the desired stoichiometry and hence the desired combination of properties, e.g. electrical conductivity, corrosion resistance etc. It is possible to apply a mixture of the suboxides or just a single one. Most preferably the plasma spraying of the defined titanium suboxide is carried out under conditions which preclude the risk that the stoichiometry will be affected. To this end the application for example may be carried out under vacuum or under a shield of a suitable inert gas, e.g. argon.

It is advantageous to pretreat the surface of the substrate to enhance the adhesion of the applied coating. The pretreatment may be mechanical, chemical or electrochemical, e.g. sand/grit blasting, deposition, laser ablation, etching, stove coating; or the like.

The method may include the variation of adding minor properties of a dopant to the material to be applied. Examples include electrocatalysts and other stabilisers, e.g. Pt, Ir, Ta, Nb, Ru, V; and the like; and oxides, e.g. tin oxide and mixtures thereof. These may influence conductivity, adhesion, corrosion resistance properties. Typically the composition will be in particulate form, e.g. a powder. Such additions may be made as a subsequent treatment, e.g. a further coating of an electrocatalyst may be applied by electroplating, thermal stove-coating, or the like to influence the electrochemical properties of the end product.

The application equipment, e.g. plasma gun, may be of known type with appropriate additional attachments to ensure an inert gas blanket, e.g. as described in GB-A-2281488.

The laser will be adapted to melt the powder en route to the substrate, but is particularly efficacious since it can be operated in a more complete vacuum or purer inert gas atmosphere. In addition it is possible to clean the surface of the substrate to be coated by a laser surface ablation technique wherein a second laser process can deliver a high energy pulse (typically 35MW over 20 nS) to blast away surface oxides and other contaminants from the substrate immediately prior to the arrival of the molten powder.

The coated item can be used as an electrode (either anode or cathode) in low current density applications directly, or where necessary for high current density with the application of a suitable electrocatalyst as noted above. The surface may also be electroplated with, for instance, lead or zinc metals to assist electrical connectivity to or adhesion of active materials in a battery. The electrode may be used in electrochemical cells, metal winning, chlorine cells, effluent treatment; and the like.

The method allows coatings to be applied up to thicknesses well in excess of those required for corrosion resistance alone, whilst maintaining good conductivities. The coating thickness may range from about 50 to about 1000×10^{-3} mm. For very high corrosion resistances a typical coating would be either of the order of $200-500 \times 10^{-3}$ mm where x is about 1.75 to 1.8, or a thinner coating of about $100-200 \times 10^{-3}$ of a stoichiometry where x is about 1.85 to 1.9. For less arduous duty, high conductivity coatings of about $100-200 \times 10^{-3}$ mm and a stoichiometry of $x = 1.75-1.8$ are preferred. A coating of the invention will have conductivity of the order of 10 to 100 S/cm. In even less arduous corrosion duty, dopants can be added which further increase the conductivity.

In order that the invention may be well understood it will now be described with reference to the following examples which are given by way of illustration only.

EXAMPLE I

Test electrodes for electrowinning of zinc were prepared in the following manner. Two sheets of commercial grade aluminium 2 mm thick and 230 x 80 mm width and breadth, were lightly filed around all edges to remove sharp edges and burrs, and then grit blasted. The items were then plasma sprayed using a Metco gun equipped with a

Shroud as described in GB-A-2281488 which was controlled by a robot which ensured an even coating over the entire surface and edges. The gun was fed with a pre-prepared powder of whose stoichiometry had been measured by X-ray diffraction as being as of composition TiO_x where $x = 1.72$. The conductivity was found to be 10S/cm. The coating was found to be 120 microns thick, with a bulk density of 3.84 gm/cc. Subsequently adjustments were made to the argon and hydrogen flowrates and pressures and a stoichiometry of TiO_x where $x = 1.76$ was obtained, and a bulk density of 4.03 gm/cc obtained. (It is generally accepted that if the bulk density is within 5% of the theoretical full density, then no interconnected porosity is present).

The coated anode was further treated with an electrocatalytic coating based on mixed oxides of tantalum and iridium. During the stove coating, one of the test electrodes lost a high proportion of its coating due to the thermal expansion difference between the ceramic and metallic components and was discarded. However, the other survived temperature cycling to about 400°C through 30 coats. This anode was used in a test cell as an anode in the electrodeposition of zinc from a solution of 50 gm/litres Zn^{2+} and 180–200 gm/litre H_2SO_4 with traces of fluoride, (~ 10 mg/litre) Mn^{2+} (5–8 mg/litre) and other contaminant materials found in a commercial zinc electrowinning stream, performing successfully at a current density of 450A/m² for over 1000 hours of operation. It was notable in this test that although the electrode potential did rise from an initially low (and preferred) level, in the long term, the anode had a potential of about 250mV lower than the Pb/Ag anode material more conventionally used, and that any MnO_2 which formed on the anode fell off of its own accord from time to time or could be assisted by occasional ultrasonic treatment.

EXAMPLE II

Token pieces of titanium metal were coated by the process of Example I. Because of the smaller difference between the expansion coefficients of the metal and the coating, they were stove coated with electrocatalysts without any spalling of the coating layer.

EXAMPLE III

Solid pieces and expanded metal meshes of aluminium and of titanium were coated with conductive ceramic by the method of Example I and then electrocoated at modest temperatures with lead dioxide, platinum metal, and antimony/tin oxide coatings.

EXAMPLE IV

Conductive ceramic coatings were applied using the method of Example I to test pieces made of steel, brass, copper, lead and KEVLAR (which is not metallic).

CLAIMS

1. A method of forming a corrosion resistant electrically conductive coating on a substrate, comprising forming a predetermined titanium suboxide of the formula TiO_x where x is 1.55 to 1.95 and then applying that material on to the substrate to form a coating of substantially the same stoichiometry on the substrate.
2. A method according to Claim 1, wherein the material is applied by plasma spraying.
3. A method according to Claim 1, wherein the material is applied by laser coating.
4. A method according to Claim 1, wherein the material is applied by a de-gun coating technique.
5. A method according to Claim 1, 2, 3, or 4, including adding a dopant to the titanium suboxide and applying that doped composition on to the substrate.
6. A method according to Claim 5, wherein the dopant is an electrocatalyst and/or other stabiliser.
7. A method according to any preceding Claim, wherein the coating is applied to a thickness of the order of $50\text{-}1000 \times 10^{-3}$ mm.

8. A method according to any preceding Claim, including the preliminary step of treating the surface of the substrate by mechanical, laser, chemical or electrochemical treatment before the composition is applied thereon.
9. A method according to Claim 8, wherein the pretreatment is blasting, chemical or deposition; stove coating; or the like.
10. A method according to any preceding Claim, wherein the application of the material is carried out under vacuum.
11. A method according to Claim 10, wherein the application of the material is carried out in an atmosphere comprising a gas selected to exclude ingredients which will affect the titanium suboxide.
12. A method according to Claim 11, wherein the gas is argon.
13. A method according to any preceding Claim, including the subsequent step of applying an electrocatalytic material, whereby the surface is further coated with an electrocatalyst including precious metals, mixtures thereof and their oxides and mixtures thereof, lead dioxide, doped tin oxide and the like.
14. A method according to any preceding Claim, wherein the substrate comprises an electrode for an electrochemical cell.



Application No: GB 9701229.8
Claims searched: 1-14

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Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C7F (FGA, FGZ, FLA); C7B (BEDH, BEDJ, BEDN, BEDT); B2E
EBDA, EBDB)

Int Cl (Ed.6): C23C (4/10, 4/12, 26/00, 26/02); C04B 35/46; C25B 11/04; B05D (1/08,
5/10, 5/12)

Other: Online: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1595061 (UKAEA) see esp exs	1,2
X	GB 1464375 (AEL) see esp p2 lines 3-90	1,2
X	GB 1438462 (HOECHST) see esp ex 1	1,2
X	US 5538612 (NGK) see esp claim 1 & col4 lines 39-45	1
X	US 5521029 (AT & T) see esp col4 lines 10-21	1
X	US 5225382 (NISSHIN) see esp col2 line 63 - col3 line 2	1
X	US 4898785 (PLASMAINVENT) see esp col4 lines 42-56	1,10
X	US 4861680 (SOUTHWALL) see esp claim 1	1
X	US 4595822 (KYOCERA) see esp cols 3-4	1
X	US 4395432 (WESTINGHOUSE) see esp ex	1,11,12
X	US 4194022 (PPG) see esp col2 line 67 - col3 line 5	1
X	US 3330707 (VARIAN) see esp col3 line 66 - col4 line 14	1

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined
with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before
the filing date of this invention.
E Patent document published on or after, but with priority date earlier
than, the filing date of this application.



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Date of search: 17 March 1997

Category	Identity of document and relevant passage	Relevant to claims
X	WPI Accession no 92-021640/03 & JP 3271386 A (DAISO) see abstract	1
X	WPI Accession no 86-031550/05 & JP 60251291 A (ISHIFUKI) see abstract	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

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